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DETERMINING TETRAFLUOROBORATES: AN EVALUATION OF FLUOROBORATE ANION SELECTIVE ELECTRODE

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The Orion fluoroborate electrode was evaluated to determine its applicability to water and waste. The calibration curve was Nernstian down to 0.6 mg/l and the slope of the curve was 56 millivolts per decade change. Interference of nitrate and sulfate was studied. Low results were obtained for samples that contained 50 mg/l of sulfate and 10 mg/l tetrafluoroborate or 10 mg/l sulfate and 1 mg/l tetrafluoroborate. To determine 1 mg/l of tetrafluoroborate, nitrate should be absent. The fluoroborate electrode can be used directly to determine some selected fluoroborates.

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DETERMINING TETRAFLUOROBORATES: AN EVALUATION OF THE FLUOROBORATE ANION SELECTIVE ELECTRODE

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

There is an ever-increasing interest in the use of electrode methods to analyze water and waste samples, whether the resulting data are to be used for research, surveillance, compliance monitoring, or enforcement purposes. Accordingly, the Environmental Monitoring and Support Laboratory has an on-going methods research effort in the development, evaluation, and modification of electrode procedures. This particular report pertains to the evaluation of fluoroborate electrode. The method has potential routine application for the analysis of fluoroborates in surface waters and domestic and industrial wastes.

Dwight G. Ballinger, Director
Environmental Monitoring and Support Laboratory
Cincinnati

ABSTRACT

Tetrafluoroborates (BF_4^-) are being used in the plating industry in place of cyanide. These compounds are highly desirable because they eliminate the use of cyanide. The tetrafluoroborate electrode was applied to fluoroborate measurements in electroplating bath samples.

The tetrafluoroborate electrode was evaluated for response time, reproducibility, Nerstian behavior, possible potential interferents, and accuracy. The electrode technique was compared with the SPADNS colorimetric technique for fluoride analysis. The feasibility of using the fluoroborate electrode and fluoride electrode to observe hydrolysis was studied.

The tetrafluoroborate electrode was reproducible, with response time around 6 seconds. Possible potential interferents included perchlorate, iodide, nitrate, and sulfate. In the case of nitrate and sulfate, concentrations of 1 and 10 ppm tetrafluoroborate were studied, as was the effect of pH. The fluoride electrode technique, tetrafluoroborate electrode technique, and SPADNS colorimetric technique were compared. With distillation, the colorimetric analysis gave 98% recovery in comparsion with 90% recovery for fluoride electrode analysis. By subtracting the fluoride content before distillation from the total fluoride determined colorimetrically, the amount of fluoride from the tetrafluoroborate may be determined. The tetrafluoroborate electrode can be used directly in electroplating baths to determine some selected fluoroborates. The standard addition method was also studied.

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SECTION I

INTRODUCTION

In the plating industry, tetrafluoroborate has been used in place of cyanide in electroplating baths. These tetrafluoroborate baths have many advantages over cyanide baths: no severe waste disposal problems and no handling of dangerous, highly toxic cyanide. However, hydrolysis occurs giving rise to fluoride as waste in tetrafluoroborate solutions.

Preliminary investigations have shown that tetrafluoroborates break down to fluoride ions in the Bellack fluoride distillation. An ion-selective electrode technique that is capable of determining tetrafluoroborate ions at low concentrations requires less preparation, eliminates the distillation step and would find use in the water pollution control field. The tetrafluoroborate electrode capability would also save time, require less sample volume and fewer chemical reagents.

This project was divided into three phases. Phase one involved: (a) evaluation of reproducibility and response time, (b) preparation of calibration curves, and (c) evaluation of interferences for the fluoroborate electrode. In phase two, a colorimetric method was compared with the fluoride and fluoroborate electrode methods. In phase three, the feasibility of using fluoride and fluoroborate electrodes to observe the hydrolysis of fluoroborate was investigated.

SECTION II

CONCLUSIONS

The tetrafluoroborate electrode was evaluated for response time, reproducibility, and Nernstian-like behavior. The time required for the electrode to reach a relatively stable potential, as indicated by a recorder curve, was around 6 seconds for decade changes in fluoroborate concentrations. The reproducibility of the electrode depended on the concentration. As the concentration of tetrafluoroborate decreased, the standard deviation became higher with regard to a calibration curve. The Nernstian-like behavior for the tetrafluoroborate gave a slope around 56 millivolts down to about 0.6 ppm tetrafluoroborate.

The greatest interferents appeared to be perchlorate, nitrate, and iodide. Sulfate also interfered. Lower results would be obtained for samples containing more than 10 ppm sulfate in 1 ppm tetrafluoroborate. In 1 ppm tetrafluoroborate, nitrate should be absent for accurate results. The pH showed little effect on concentrations of 1 and 10 ppm of tetrafluoroborate. But, it may affect the sample if the pH is greater than 6 for 100 ppm tetrafluoroborate. Due to the interference of nitrate, the tetrafluoroborate electrode may not be useful in river water.

The colorimetric method appeared to give the best recovery of total fluoride from tetrafluoroborate. Ninety percent recovery was obtained with the fluoride electrode method whereas 98% was recovered with the SPADNS colorimetric method. The fluoride electrode method and the tetrafluoroborate electrode can be used before distillation in pure sodium tetrafluoroborate to determine the amount of fluoride coming from the tetrafluoroborate. The amount of fluoride measured with the electrode before distillation was subtracted from the total fluoride obtained. The use of the colorimetric method for fluoride content before distillation was not practical because of the speed of hydrolysis. Copper and lead fluoroborate compared favorably with all methods whereas tin and 60% tin - 40% lead mixture did not. The results from the fluoroborate electrode were low for tin fluoroborate, and this would be expected if there were some strong complexation. However, the tetrafluoroborate electrode should not be used directly in the presence of interferents or complexed fluoroborate ions. It might be possible to use the standard addition method.

The use of the fluoride and fluoroborate electrodes to measure the rate of hydrolysis may be feasible with an appropriate buffer solution. A buffer solution should be found that would not interfere with the hydrolysis and measuring devices. Without a buffer system, the hydrolysis determinations would be cumbersome with the two electrodes.

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SECTION III

RECOMMENDATIONS

1 The tetrafluoroborate electrode can be used to determine tetrafluoroborate in electroplating baths. However, it is advisable that a colorimetric analysis be performed initially for comparison purposes. In using the colorimetric analysis for total fluoride content, the fluoride content before the analysis should be subtracted before calculating the amount of tetrafluoroborate.

2 Further studies should also be made on the hydrolysis reaction and rates of tetrafluoroborates.

3 It is recommended that a study be made on the possible automation of the distillation and analysis of tetrafluoroborates.

4 It is recommended that further investigations be made on the complexation of tetrafluoroborate.

SECTION IV

EXPERIMENTAL

PHASE I

A. Preparation of Standard Solutions

Stock solutions of 10^{-1} M sodium tetraflurooborate (Alpha Inorganic Inc.) were made by dissolving 10.9790 grams in approximately 100 ml of de-ionized water and filtered. The filtrate was transferred to one liter volumetric flask and diluted to the mark with de-ionized water. The stock solution was kept about five days due to hydrolysis.

A stock solution of 10^{-1} M sodium fluoride was prepared by dissolving 4.1990 grams in one liter of de-ionized water.

Stock solutions of 1000 ppm sodium tetrafluoroborate were made essentially the same as above with the exception that 1.264822 grams were dissolved in approximately 100 ml of distilled water. A stock solution of 100 ppm sodium fluoride was prepared by dissolving 0.221023 grams in one liter of distilled water.

All reagents were used without further purification. Sodium fluoride and sodium tetrafluoroborate were dried in an oven at 110°C for 24 hours. The stock solutions were stored in polyethylene bottles in a water bath at 25°C. From the stock solutions, standard solutions were made by serial dilution each day.

B. Measurements

Electrode potentials measurements were made on an Orion model 801A ionalyzer. The solutions were magnetically stirred at a constant, slow rate using a Teflon-coated stirring bar, and EMF readings were taken after six minutes as indicated by the Orion model 751 printer. The Orion model 92-05 fluoroborate and model 94-09 fluoride specific ion electrodes were used with a single junction reference electrode.

The Orion model 90-91 single junction reference electrode was filled with 0.1 M potassium chloride saturated with silver chloride.

PHASE II

A. Preparation of Tetrafluoroborates

Stock solutions of 1000 ppm sodium tetrafluoroborate (Alpha Inorganic Inc.) were made by dissolving 1.264832 grams in approximately 100 ml of distilled water and filtered. The filtrate was

transferred to one liter volumetric flask and diluted to the mark with distilled water. From the stock solutions, 4 ppm tetrafluoroborate were made each day.

From the pint sample bottles, 2 ml were diluted to one liter. Then, subsequential dilutions of 3 ml of the 2 cc/l were diluted to 500 ml with distilled water each day. These methods were used to make the cupric, stannous and lead tetrafluoroborate solutions. The sixty-forty mixtures were made by taking 200 ml of the 3 cc/500 ml lead tetrafluoroborate and diluting to the mark of 500 ml with 3 cc/500 ml of tin tetrafluoroborate. This gave a 60% tin and 40% lead tetrafluoroborate.

B. Preliminary Distillation

1. Apparatus

Corning No. 3360

2. Procedure

a. Place 400 ml distilled water in the distilling flask and carefully add 200 ml concentrated sulfuric acid, H_2SO_4. Swirl until the flask contents are homogeneous. Add 25-35 glass beads. Begin heating slowly at first, then as rapidly as the efficiency of the condenser will permit (the distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process served to remove fluoride contamination and to adjust the acid-water ratio for subsequent distillation.

b. After cooling the acid mixture remaining from steps outlined in (a), or previous distillations, to 120°C or below, add 300 ml of sample, mix thoroughly, and distill as before until the temperature reaches 180°C. To prevent sulfate carry-over, do not permit the temperature to exceed 180°C.

c. After distillation of fluoride, flush the still with 300 ml distilled water.

C. Electrode Method

1. Apparatus

a. Orion Model 801A ionalyzer

b. Single junction reference electrode

c. Fluoride electrode, Orion Model 94-09

2. Reagents

a. Stock fluoride solution: Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in distilled water and dilute to one liter (100 ppm fluoride).

b. Standard fluoride solution: Dilute 100 ml stock fluoride solution to one liter (10 ppm fluoride).

c. Total ionic strength adjustment buffer (TISAB). Place approximately 500 ml distilled water in a one liter beaker. Add 57 ml concentrated (glacial) acetic acid, 58 g sodium chloride, NaCl, and 12 g sodium citrate dihydrate, $Na_3C_6H_5O_7 \cdot 2H_2O$. Stir to dissolve. Place the beaker in a water bath (for cooling), insert a calibrated pH electrode and reference electrode into the solution and slowly add approximately 6 N sodium hydroxide (about 125 ml) until the pH is between 5.0 and 5.5. Cool to room temperature. Put into a one liter volumetric flask and add distilled water to the mark.

3. Procedure

a. Preparation of fluoride standards and standard curve: Measure 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0, ml standard fluoride solution into a series of 100 ml volumetric flasks to produce fluoride concentrations of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1.0 mg/l. To each flask, add by pipet 50 ml TISAB solution and dilute to 100 ml with distilled water. Mix well.

b. Preparation of Standard Curve.
The solutions above were measured in duplicates and the average calculated. A plot of EMF versus part per million fluoride was made.

D. Colorimetric Method

1. Apparatus

Coleman Model 124 Double Beam Spectrophotometer

2. Reagents

a. Standard fluoride solution: Prepared essentially as directed in the electrode method.

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b. SPADNS solution: Dissolve 958 mg SPADNS, sodium 2 (para sulfophenylazo)-1, 8 - dihydroxy - 3, 6 - naphthalene disulfonate, also called 4,5-dihydroxy -3-(para sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, in distilled water and dilute to 500 ml. This solution is stable indefinitely if protected from direct sunlight. It was stored in a brown bottle.

c. Zirconyl-acid reagent: Dissolve 133 mg Zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in about 25 ml distilled water. Add 350 ml concentrated HCL and dilute to 500 ml with distilled water.

d. Acid Zirconyl - SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl - acid reagent to produce a single reagent, which is stable for at least 2 yrs.

3. Procedure

a. Preparation of Standard Curve:
Prepare fluoride standards in the range of 0 to 1.40 mg/l by diluting appropriate quantities of the standard fluoride solution to 50 ml with distilled water. Pipet 10.00 ml of the mixed acid-zirconyl-SPADNS reagent to each standard and mix well, exercising care to avoid contamination during the process. Set the spectrophotometer to zero absorbance with distilled water in both curvettes. Use distilled water as the reference solution. Plot a curve of the fluoride concentration -absorbance relationship at 570 nm.

E. Sampling

For the electrode method, the distillate or distillant (50 ml) was diluted to the mark in a 100 ml volumetric flask with TISAB. For the colorimetric method, the distillate (5 ml) was diluted to 100 ml with distilled water. In the case of sodium fluoride, the distillate or distillant (100 ml) was used. The samples were measured in duplicates and averaged. This process was carried out in triplicates.

F. Standard Addition Method

To 100 ml of sample, one milliliter of 100 ppm sodium tetrafluoroborate was added. The electrode potentials were measured before and after the addition. Only in the case of sodium tetrafluoroborate was two milliliters of 1000 ppm sodium tetrafluoroborate added.

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PHASE III

Calibration

A calibration curve was made for tetrafluoroborate at 0.5, 1.0, 5.0, 10.0, and 100 ppm in a polyethylene thermostatic water jacketed cell at 40°C. A calibration curve was also made for fluoride at 0.01, 0.1, 1.0, and 10.0 ppm fluoride at 40°C. The pH meter was calibrated at 40°C with a buffer solution.

Hydrolysis

Water (100 ml) at 40°C was placed in the cell and an aliquot equal to the aliquot to be added was removed. The electrodes were immersed, and the aliquot added. The electrodes were placed in the 40°C solution intermittently, and the measurements were taken intermittently as measured by the printer. Standards were measured before intermittent readings. Four ppm tetrafluoroborate were used. Later, 8 ppm were used in unbuffered solutions.

SECTION V

DISCUSSION

PHASE I

Reproducibility and Response Time

Tetrafluoroborate solutions (10^{-3}M) were freshly prepared five times and read in duplicates. The standard deviation obtained for a concentration of 10^{-3}M was 0.27.

The dynamic response time was obtained by adding with a plastic syringe one ml of a more concentrated solution to a rapid stirred solution to give the desired decade change. In the case of the decade change in concentration of 10^{-4} to 10^{-3}M, one cc of 9.1×10^{-2}M sodium tetrafluoroborate ($NaBF_4$) was added. The time required to reach a relatively stable potential as indicated by a recorder curve was around six seconds for decade changes in fluoroborate concentrations. For the fluoride electrode, the response time for a decade change in concentration was somewhat slower than fluoroborate electrode. The response time for a decade change of 10^{-4} to 10^{-3}M was about 17.0 seconds.

Calibration Curve

A plot of potential against the logarithm of the concentration of fluoride and fluoroborate was made from data in Tables 1 and 2. Potentials were measured in replicates with averages and standard deviations calculated. According to the equations below, the slope of the calibration curves (1) should be 59.16 millivolts per decade.

$$E = E' - 2.3 \frac{RT}{F} \log a_{BF_4^-} \qquad (1)$$

$$E = E' - 2.3 \frac{RT}{F} \log a_{F^-} \qquad (2)$$

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Where

E = the measured total potential of the system.

E' = the portion of the total potential due to choice of external reference electrodes and internal solutions.

Table 1. POTENTIALS VERSUS CONCENTRATION OF TETRAFLUOROBORATE

Concentration, ppm	mv_1	mv_2	mv_3	mv_4	mv_5	mv_6	Average	Standard Deviation
0.1	198.9	202.7	221.2	209.8	213.2	208.6	209.0	7.9
1.0	176.8	176.3	180.2	176.7	180.0	177.9	178.0	1.7
Calculated ppm	1.08	1.10	0.94	1.08	0.94	1.03	1.03	± 0.07
10.0	123.1	122.9	124.4	123.8	124.3	123.3	123.6	0.6
Calculated ppm	9.69	9.77	9.63	9.42	9.23	9.61	9.58	± 0.2
100.0	65.7	65.2	65.4	64.9	65.4	65.1	65.3	0.3
Calculated ppm	101.50	103.60	102.76	104.98	102.76	104.03	103.20	± 1.2
1000.0	10.0	10.2	9.6	9.6	9.8	10.0	9.9	0.2
Calculated ppm	991.70	983.60	1008.06	1008.06	999.85	991.70	997.00	± 9.7

Table 2. POTENTIALS VERSUS CONCENTRATION OF FLUORIDE

Concentration, ppm	mv_1	mv_2	mv_3	mv_4	mv_5	mv_6	Average	Standard Deviation
0.01	136.0	129.5	135.7	134.1	137.9	135.5	134.8	2.9
0.10	84.9	83.7	84.4	84.0	85.7	84.7	84.6	0.7
1.00	25.6	24.3	24.9	25.8	27.9	26.6	25.9	1.3
10.00	-32.4	-33.2	-32.7	-32.7	-39.9	-31.8	-32.3	0.8
100.00	-90.1	-90.5	-89.6	-90.3	-89.7	-89.3	-89.8	0.7

$2.3 \frac{RT}{F}$ = nernst factor (59.16 mv at 25°C). R and F are constants and T is the temperature in degrees Kelvin

$a_{BF_4^-}$ = the fluoroborate ion activy in the sample solution.

a_{F^-} = the fluoride ion activity in the sample solution.

The Nernstian-like behavior, illustrated in Figures 1 and 2, gave a slope around 58 millivolts for fluoride electrode and 56 millivolts for fluoroborate electrode. The lower curvature for fluoroborate electrode was probably caused by the water solubility of the ion exchanger.

Interferences

The electrode responds to certain other anions as well as fluoroborate ions. The selectivity constants (1,2,3,4,5) were calculated by two methods. Measurements were made in duplicates and averaged. The selectivity for one ion over another is expressed in equation number 3.

$$E = E^{\circ} - 2.3 \frac{RT}{F} \log (a_A + K_{A,B} a_B) \qquad (3)$$

Where a_A = activity of ion BF_4^-

a_B = activity of interferent ion B

$K_{A,B}$ = selectivity constant

When measurements are made in two solutions each containing the sodium cation only at a concentration of 10^{-3}M, then

$$E(MB) - E(MA) = -2.3 \frac{RT}{F} \log K_{A,B} (a_B / a_A) \qquad (4)$$

hence the selectivity constant can be determined as (a_B / a_A) approximately equal to one. Results are shown in Table 3.

For the univalent anions, perchlorate, nitrate, and iodide appear to be

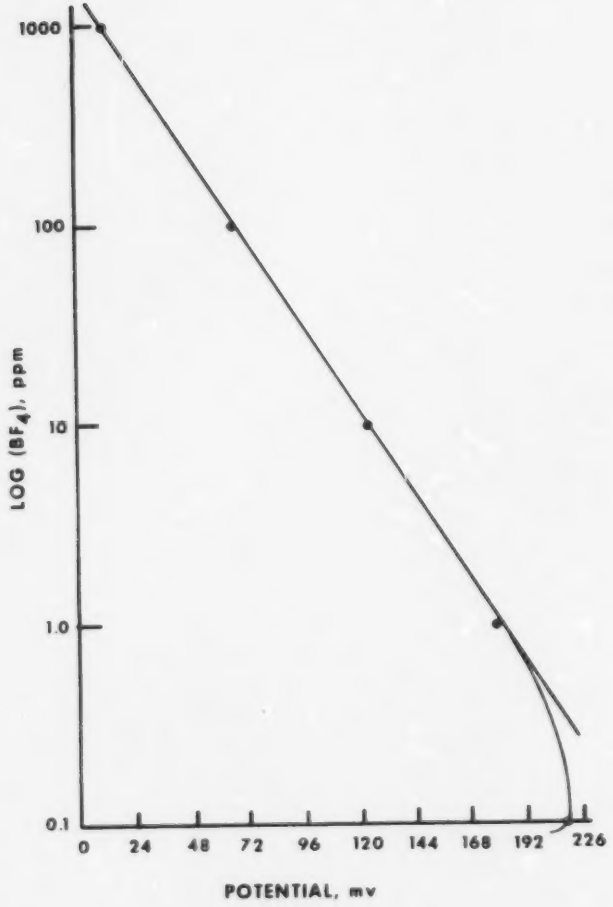

FIGURE 1.

CALIBRATION-CURVE FOR TETRAFLUOROBORATE

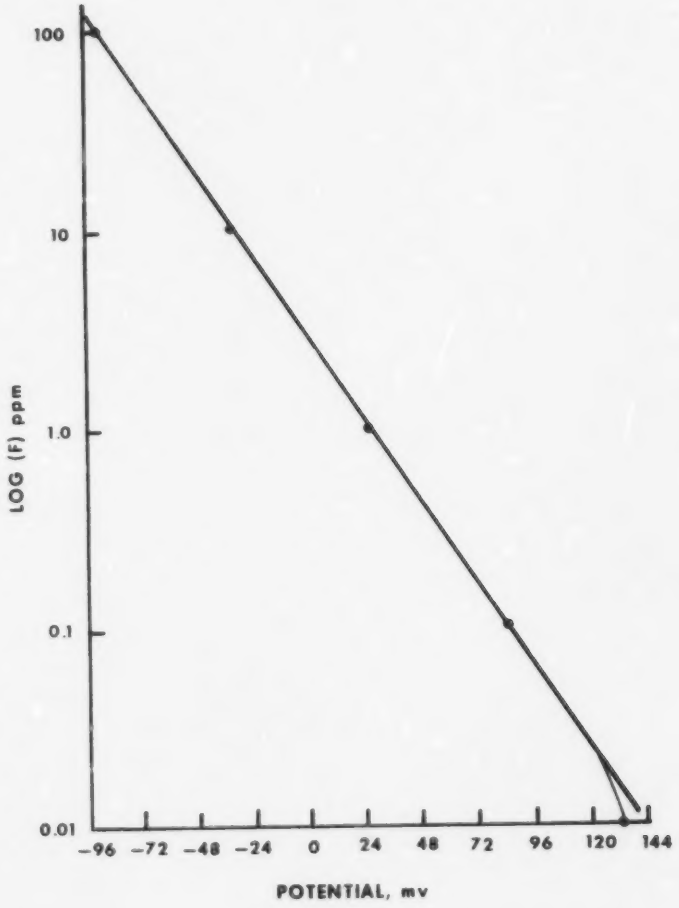

FIGURE 2.

CALIBRATION-CURVE FOR FLUORIDE

Table 3. SELECTIVITY CONSTANTS FOR FLUOROBORATE ELECTRODE

(Method 1)

Interferent Ion	Difference	K
ClO_4^-	-42.65	5.25
Ac^- (acetate)	139.60	4.37×10^{-3}
F^-	154.40	2.46×10^{-3}
Cl^-	146.55	3.33×10^{-3}
Br	118.95	9.76×10^{-3}
I^-	55.75	1.14×10^{-1}
NO_3^-	96.75	2.32×10^{-2}

the greatest interferents for the fluoroborate electrode.

The second method for calculating the selectivity constants involves a constant concentration of 10^{-3} interferent ion and a decade change of fluoroborate (10^{-3} and 10^{-4}M) ion. In other words, two different solutions with a decade change in fluoroborate ion concentrations and same level of interferent ion concentration were measured. The selectivity constant was expressed in equation number 5.

$$K = \frac{a_{1BF_4^-} \Theta a_{2\ BF_4^-}}{\Theta\ a_i 1/z_i - a_i\ 1/z_i} \qquad (5)$$

where

$a_{1\ BF_4^-}$ = activity of fluoroborate in solution one.

$a_{2\ BF_4^-}$ = activity of fluoroborate in solution two.

$a_{1\ 1/z_i}$ = activity of interferent ion with anionic charge z_i.

θ = $(E_2-E_1)\ F/RT$

Activity coefficients were calculated from the Debye Huckel Limiting Law equation (6). Results of method 2 are shown below in Table 4.

Table 4. SELECTIVITY CONSTANTS FOR FLUOROBORATE ELECTRODE

(Method 2)

Interferent Ion	Difference	K
Metaborate ($B_2O_4^=$)	57.45	3.53×10^{-3}
Borate ($B_4O_7^=$)	58.60	3.53×10^{-3}
Citrate ($C_6H_5O_7^{\equiv}$)	58.65	1.26×10^{-3}
Tartrate ($C_4H_4O_6^=$)	58.85	3.52×10^{-3}
Phosphate ($PO_4^{\equiv}$)	58.20	1.27×10^{-3}
Sulfate ($SO_4^=$)	60.30	3.53×10^{-3}

A correlation of sulfate levels with tetrafluoroborate concentrations was made. (See Table 5). The greatest potential difference between the standard solution and the solutions containing both the 10 ppm tetrafluoroborate and sulfate concentrations was 1.8 mv. From the calibration curve, a difference of 3.9 mv gave 9.0 ppm tetrafluoroborate. This indicated an error around ten percent for the 10 ppm level of tetrafluoroborate. For the one part per million tetrafluoroborate , the error was somewhat larger as would be expected from the standard deviation given in Table 1. From the data, it is indicated that lower results will be obtained for samples that contain more than 50 ppm sulfate in 10 ppm tetrafluoroborate. Also, lower results will be obtained for samples that

Table 5. CORRELATION OF SULFATE LEVELS WITH TETRAFLUOROBORATE CONCENTRATIONS

		Calculated
10 ppm of Tetrafluoroborate	124.0 mv	9.34 ppm
1.0 ppm of Tetrafluoroborate	178.0 mv	1.025 ppm

Sulfate Concentration (ppm)	In 10 ppm BF_4^-		In 1.0 ppm BF_4^-	
	mv	Difference	mv	Difference
250	125.8	1.8	183.6	5.6
Calculated ppm of BF_4^-	8.67	- 1.33	0.81	- 0.19
150	125.6	1.6	183.3	5.3
Calculated ppm of BF_4^-	8.70	- 1.30	0.82	- 0.18
50	125.0	1.0	183.0	5.0
Calculated ppm of BF_4^-	8.92	- 1.08	0.83	- 0.17
10	123.7	0.3	181.9	3.9
Calculated ppm of BF_4^-	9.40	- 0.6	0.87	- 0.13
1	123.2	0.8	179.4	1.4
Calculated ppm of BF_4^-	9.60	- 0.4	0.96	- 0.04
0.1	123.2	0.8	178.9	0.9
Calculated ppm of BF_4^-	9.60	- 0.4	0.98	- 0.02

contain more than 10 ppm sulfate in 1 ppm tetrafluoroborate.

A correlation of nitrate levels with tetrafluoroborate concentrations is shown in Table 6. From the table, it was noted that interference was greater for lower concentrations of tetrafluoroborate than for higher concentrations. It can also be seen that as the concentration of the interfering nitrate increased, the error increased. For 1 ppm tetrafluoroborate, nitrate should be absent for accurate results.

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Table 6. CORRELATION OF NITRATE LEVELS WITH TETRAFLUOROBORATE CONCENTRATIONS

10 ppm of Tetrafluoroborate 124.0 mv
1.0 ppm of Tetrafluoroborate 178.0 mv

Nitrate Concentration (ppm)	In 10 ppm BF_4^-		In 1.0 ppm BF_4^-	
	mv	Difference	mv	Difference
250	119.0	5.0	140.0	38.0
Calculated ppm of BF_4^-	11.40	+ 1.4	4.85	+ 3.85
150	120.2	3.8	142.6	35.4
Calculated ppm of BF_4^-	10.90	+ 0.9	4.36	+ 3.36
50	121.9	2.1	157.1	20.9
Calculated ppm of BF_4^-	10.10	+ 0.1	2.57	+ 2.41
10	122.5	1.5	173.0	5.0
Calculated ppm of BF_4^-	9.90	- 0.1	1.26	+ 0.25
1	122.3	1.7	174.5	3.5
Calculated ppm of BF_4^-	9.96	0.1	1.18	+ 0.18
0.1	122.7	1.3	176.9	1.1
Calculated ppm of BF_4^-	9.8	0.2	1.07	+ 0.07

Potential measurements were also made as the pH was changed. The pH was varied by adding increments of 10^{-3}M sodium hydroxide and 10^{-3}M hydrochloric acid to 100 ml of solution. Volume corrections and calibrations were made. From the data in Tables 7 and 8, Figures 3 and 4 were plotted for 1.0, 10, and 100 ppm tetrafluoroborate and fluoride, respectively. Little potential change was noted between pH 3 and pH 10 for the tetrafluoroborate concentrations. Some results may be affected if the sample is greater than pH 6 for 100 ppm tetrafluoroborate. Lower results are obtained below pH 3. For the fluoride electrode, the pH effect on the electrode response was small between pH 4 and pH 7, depending on the concentration.

Table 7. pH VERSUS POTENTIALS OF TETRAFLUOROBORATE

Concentrations (ppm)								
1.0			10			100		
pH	mv	Calculated ppm	pH	mv	Calculated ppm	pH	mv	Calculated ppm
2.00	162.9	1.89	1.99	117.4	12.20	2.00	60.9	122.90
2.15	165.6	1.69	2.15	119.2	11.30	3.01	65.2	103.60
3.19	172.4	1.04	2.98	121.7	10.20	4.13	66.0	99.80
4.16	178.6	0.99	3.48	122.1	10.00	5.06	66.4	98.20
5.20	179.0	0.98	4.84	123.0	9.67	6.07	66.8	96.60
6.20	177.1	1.06	6.34	122.3	9.96	7.23	67.7	93.00
7.00	179.1	0.97	7.51	123.5	9.48	8.95	68.1	91.00
8.02	177.1	1.06	8.84	124.0	9.29	9.78	68.3	90.80
8.97	174.5	1.18	10.11	126.9	8.25	10.72	69.6	86.50
9.98	176.5	1.08	10.99	128.5	7.73	10.81	70.0	85.00
11.06	174.0	1.20	12.02	133.0	6.70	11.08	71.0	81.70
12.01	177.4	1.04				12.01	77.6	62.40

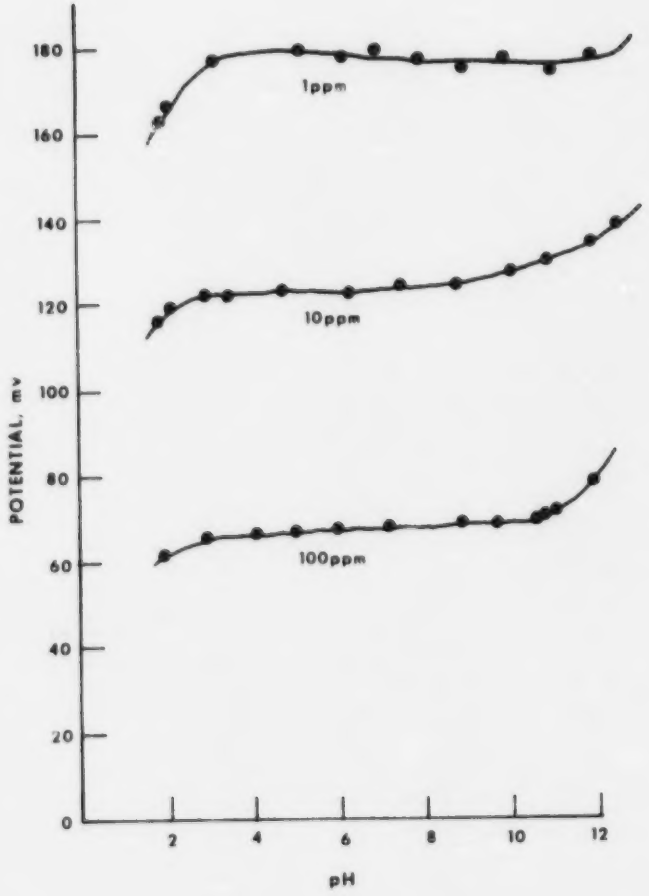

FIGURE 3.
pH RESPONSE CURVES FOR
TETRAFLUOROBORATE AT VARIOUS CONCENTRATIONS

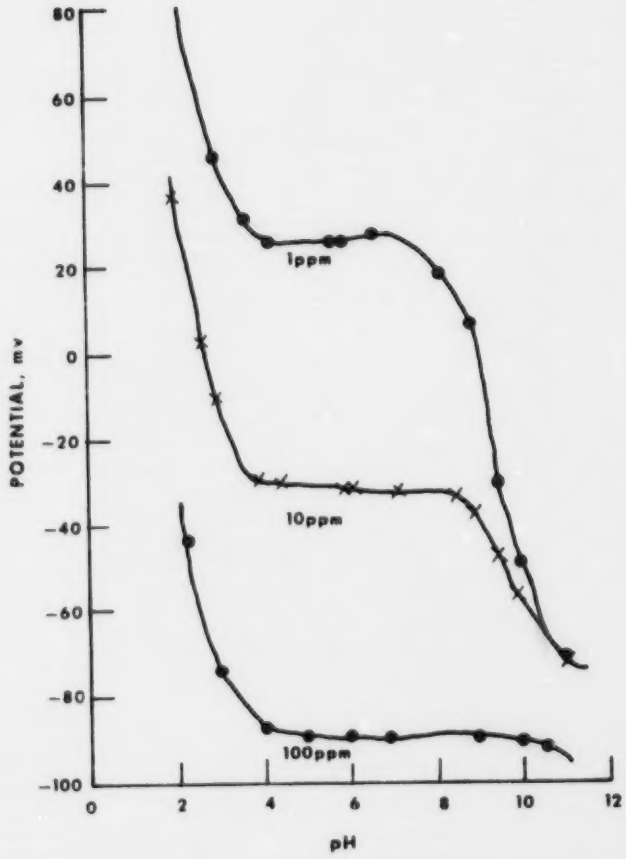

FIGURE 4.
pH RESPONSE CURVES FOR FLUORIDE
AT VARIOUS CONCENTRATIONS

Table 8. pH VERSUS POTENTIALS OF FLUORIDE

Concentration (Part-Per-Million)					
1.0 ppm		10 ppm		100 ppm	
pH	mv	pH	mv	pH	mv
2.00	89.9	2.00	35.7	2.16	-43.9
2.95	45.2	2.67	0.3	3.00	-73.8
3.57	30.8	2.94	-10.5	3.96	-88.3
4.18	25.8	3.85	-29.9	5.00	-89.8
5.78	25.9	4.39	-31.4	5.96	-89.8
5.90	25.9	5.86	-32.3	5.98	-89.8
6.56	27.2	5.95	-32.3	6.87	-89.9
8.25	17.7	7.07	-31.9	9.01	-89.8
8.90	5.6	8.53	-34.1	9.91	-90.7
9.49	-30.9	8.92	-37.9	10.51	-91.6
9.99	-48.7	9.52	-47.7		
10.51	-65.5	10.01	-57.0		
		11.12	-71.6		

SUMMARY

The response time, reproducibility, calibration curve, and interferences of the tetrafluoroborate electrode were determined. The time required to reach a relatively stable potential was around 6 seconds for decade changes in fluoroborate concentrations. The calibration curve was Nernstian-like down to about 0.6 ppm of tetrafluoroborate. The slope of the curve was around 56 millivolts for the tetrafluoroborate electrode.

The univalent anions, perchlorate, iodide, and nitrate gave the greatest interference as indicated by the calculated selectivity constants. Of the divalent anions tested, metaborate ($B_2O_4^=$), borate ($B_4O_7^=$), tartrate ($C_4H_4O_7^=$), and sulfate ($SO_4^=$) gave approximately the same selectivity constants. Further studies of the nitrate and sulfate anions in 1 and 10 ppm tetrafluoroborate gave an indication of the levels of interference. For instance, lower results than expected were obtained for samples containing more than 50 ppm sulfate in 10 ppm tetrafluoroborate. Lower results were also obtained for samples containing more than 10 ppm sulfate in 1 ppm tetrafluoroborate. In the case of the nitrates in 1 ppm tetrafluoroborate, accuracy would be obtained if nitrates were absent.

In the study of pH, higher results were obtained for samples below pH 3. Depending on the tetrafluoroborate concentration, little change in the tetrafluoroborate electrode potentials was noted between pH 3 and pH 10. However, hydrolysis was occurring rapidly between the two pH limits. This was indicated by the need to obtain the potentials of the tetrafluoroborate electrode at a specific time interval after addition of the acid or base. This also gave tetrafluoroborate the appearance of being amphoteric.

PHASE II

Calibration curves for the colorimetric method (SPADNS) and fluoride electrode methods are shown in Figures 5 and 6. The calibration curve for the fluoride was made in a solution containing the total ionic strength buffer. The curve was linear down to 0.2 ppm fluoride in the TISAB solution. The colorimetric calibration curve was linear down to 0.6 ppm fluoride or 1.3 ppm sodium fluoride. At zero fluoride concentration, this measurement was made on distilled water and the mixed colored reagent. (See Table 9.)

In Table 10, a comparison of the colorimetric method before and after distillation was made on sodium fluoride. There was essentially no difference between the average part per million fluoride before and after distillation. In relation to the fluoride electrode, there was about 4% difference. It was also noted that the fluoride electrode measurements after distillation were less than the colorimetric measurements.

Comparisons of methods for sodium tetrafluoroborate are shown in Table 11. Starting with four parts per million (ppm) tetrafluoroborate (TFB), distillation should give around 3.50 ppm fluoride. Comparing the 3.50 ppm fluoride with 3.42 ppm and 3.15 ppm, the fluoride recovered from the TFB is about 98% for colorimetric method and 90% for fluoride electrode method. The amount of fluoride was also determined before distillation (distillant). Before distillation, the fluoride content was around an average of 0.41 ppm. Calculating the fluoride content using the TFB electrode, a fluoride content of 2.98 ppm was obtained. A total fluoride content of 3.42 and 3.15 ppm was obtained by the colorimetric and fluoride electrode methods, respectively. If the amount of fluoride found before distillation was subtracted from the total fluoride content (3.42 - 0.41 = 3.01), the fluoride content from the TFB was 3.01 ppm. This gave rise to an error of one percent between the calculated amount of fluoride from the TFB electrode and the colorimetric total fluoride content minus the fluoride content measured before distillation by the fluoride electrode. On the other hand, the fluoride electrode gave 2.74 ppm fluoride from the TFB. However, this gave an error around 8% for the fluoride electrode using the same difference technique. Colorimetric analysis of the fluoride content in TFB before distillation was not possible. It was noted that within approximately two hours after the addition of the mixed reagents, the absorbance was almost identical to the TFB solution after distillation. This may be caused by the zirconium and hydrochloric acid mixture which may speed up the hydrolysis process. However, it may be possible to make colorimetric measurements on TFB solutions at quick specific time intervals. The amount of fluoride before distillation became larger as the TFB solution ages. However, a fresh stock solution and subsequential dilutions gave around 0.18 ppm fluoride before distillation.

Table 9. DATA FOR CALIBRATION CURVES

Fluoride Concentration (ppm)	Absorbance	Potentials (MV)
Blank	0.751	
0.1	0.720	101.0
0.2	0.687	84.9
0.3	0.651	74.8
0.4	0.621	67.3
0.5	0.590	62.0
0.6	0.562	57.2
0.8	0.521	49.5
1.0		43.6
5.0		1.9
10.0		-15.4

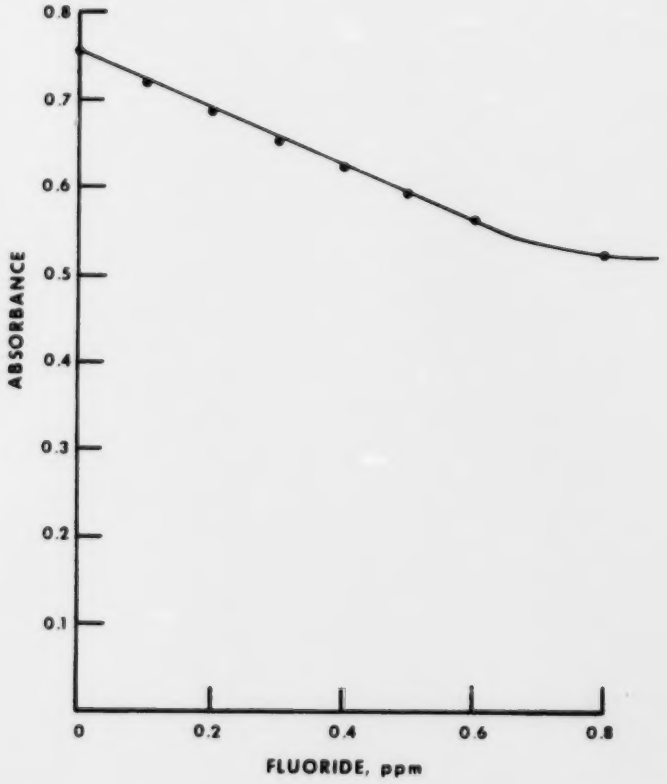

FIGURE 5.
COLORIMETRIC CALIBRATIONS CURVE
FOR FLUORIDE

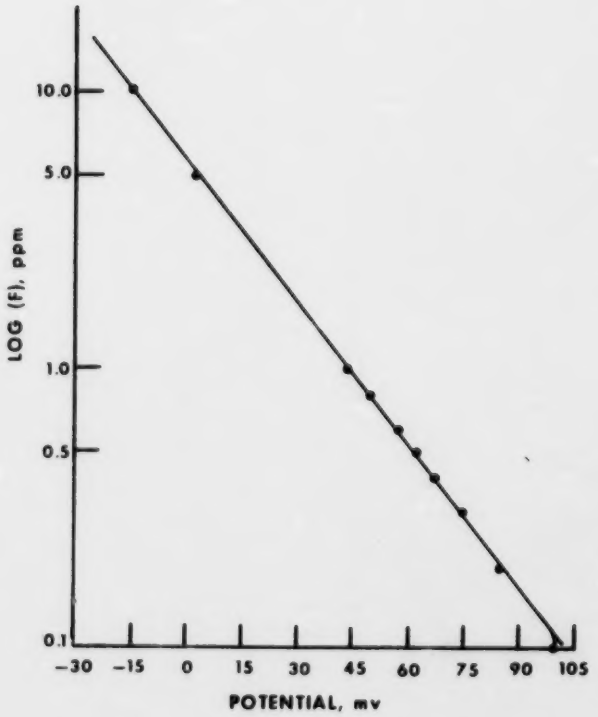

FIGURE 6.
CALIBRATION CURVE FOR FLUORIDE IN TISAB

Table 10. COMPARISON OF METHODS FOR SODIUM FLUORIDE

Before Distillation

Absorbance	From Curve	Distillant Concentration	Average Standard Deviation
0.665	0.265	0.53	0.53 ± 0.01
0.667	0.260	0.52	
0.665	0.265	0.53	

After Distillation

Absorbance	From Curve	Distillate Concentration	Average Standard Deviation
0.664	0.265	0.53	0.52 ± 0.02
0.665	0.265	0.53	
0.670	0.250	0.50	

Fluoride Electrode After Distillation

MV	From Curve	Distillate Concentration	Average Standard Deviation
77.7	0.270	0.54	0.50 ± 0.04
81.5	0.232	0.46	
79.8	0.250	0.50	

Table 11. COMPARISON OF METHODS FOR SODIUM TETRAFLUOROBORATE

Tetrafluoroborate Electrode

MV	From Curve	Average Standard Deviation
149.1	3.4	3.40 ± 0.10
148.8	3.5	
149.6	3.3	

Colorimetric Method

Absorbance	From Curve	Distillate (F^-) Concentration	Average Standard Deviation
0.640	0.340	3.40	3.42 ± 0.03
0.638	0.345	3.45	
0.640	0.340	3.40	

Fluoride Electrode

MV	From Curve	Distillate Concentration	Average Standard Deviation
32.1	1.58	3.15	3.15 ± 0.05
31.6	1.60	3.20	
32.6	1.55	3.10	

Fluoride Electrode Before Distillation

MV	From Curve	Distillant (F^-) Concentration	Average Standard Deviation
82.5	0.22	0.44	0.41 ± 0.22
74.9	0.31	0.62	
105.0	0.09	0.18	

Copper, tin, lead and 60% tin - 40% lead TFB results are shown in Tables 12, 13, 14, and 15, respectively. Using the difference technique, tin and the 60-40 mixture gave the largest errors in fluoride content. These errors were greater than 10%. Any metal in the electromotive series will displace a metal below it (a less active metal) from its salt in water solution. Considering the metals tin, lead, and copper, tin is the most active and probably will displace lead in solution. In the case of the metallic tetrafluoroborates, the measurements on the tetrafluoroborate electrode would be expected to be low if there were some strong complexing occurring. This may be the cause of the tin tetrafluoroborate potentials, as measured with the fluoroborate electrode, to be low.

A summary of the correlation of the fluoride contents is given in Table 16. It appeared as if the tetrafluoroborate electrode and the fluoride electrode could be used in some instances to determine fluoroborate and fluoride concentration in distilled water. For the case of four parts per million tetrafluoroborate, it is expected that 3.50 ppm of fluoride would be formed from four parts per million tetrafluoroborate. The tetrafluoroborate electrode gave 3.40 ppm fluoroborate which corresponds to about 2.98 ppm fluoride. The amount of fluoride present as measured with the fluoride electrode was an average of 0.41 ppm. This gave a total of 3.39 ppm fluoride from both the fluoride present and that calculated from the 3.40 ppm tetrafluoroborate. The percent difference between the expected fluoride from four ppm tetrafluoroborate and the total fluoride obtained from measurement was 3.14. However, tetrafluoroborate electrode cannot be used directly in the presence of interferents or complexed fluoroborate ions. It might be possible to use the standard addition method.

The concentration of the TFB solution used for standard addition (see Table 17) were calculated using the equation (2).

$$Cx = Cs\ (Vs/Vx + Vs)[\ 10^{E/S} - (Vx + Vs/Vx)\ ]^{-1} \quad (6)$$

Where Cs is the standard solution concentration, Cx is the unknown concentration, Vs is the volume of the standard addition aliquot, Vx is the test solution, E is the difference in potential and S is the slope. In the above equation, the slope used was 56 millivolts. The concentration calculated compared favorably with the background subtracted fluoride contents for the fluoride electrode. In Table 16, the standard addition results for sodium tetrafluoroborate cannot be compared favorably to the background subtracted fluoride concentration because the measurements were made in different standard solutions.

Table 12. COMPARISON OF METHODS FOR COPPER TETRAFLUOROBORATE

Tetrafluoroborate Electrode

MV	From Curve	Average Standard Deviation	Percentage Tetrafluoroborate
142.1	4.6	4.37 ± 0.25	36.42%
142.6	4.4		
144.5	4.1		

Colorimetric Method

Absorbance	From Curve	Distillate Concentration	Average Standard Deviation
0.590	0.495	4.95	5.18 ± 0.2
0.665	0.265	5.30	
0.664	0.265	5.30	

Fluoride Electrode

MV	From Curve	Distillate Concentration	Average Standard Deviation
20.0	2.50	5.0	5.0 ± 0.0
19.9	2.50	5.0	
20.1	2.50	5.0	

Fluoride Electrode Before Distillation

MV	From Curve	Distillant Concentration	Average Standard Deviation
58.4	0.57	1.14	1.34 ± 0.18
53.8	0.69	1.38	
51.6	0.75	1.50	

Table 13. COMPARISON OF METHODS FOR TIN TETRAFLUOROBORATE

Tetrafluoroborate Electrode

MV	From Curve	Average Standard Deviation	Percentage Tetrafluoroborate
150.4	3.3	3.07 ± 0.21	25.58%
152.2	3.0		
153.3	2.9		

Colorimetric Method

Absorbance	From Curve	Distillate Concentration	Average Standard Deviation
0.664	0.265	5.30	5.17 ± 0.23
0.673	0.245	4.90	
0.665	0.265	5.30	

Fluoride Electrode

MV	From Curve	Distillate Concentration	Average Standard Deviation
18.9	2.60	5.20	5.13 ± 0.12
18.9	2.60	5.20	
20.1	2.50	5.00	

Fluoride Electrode Before Distillation

MV	From Curve	Distillant Concentration	Average Standard Deviation
54.6	0.67	1.33	2.07 ± 0.07
40.4	1.14	2.27	
36.7	1.31	2.62	

Table 14. COMPARISON OF METHODS FOR LEAD TETRAFLUOROBORATE

Tetrafluoroborate Electrode

MV	From Curve	Average Standard Deviation	Percentage Tetrafluoroborate
143.1	4.4	4.37 ± 0.06	36.42%
143.4	4.3		
142.9	4.4		

Colorimetric Method

Absorbance	From Curve	Distillate Concentration	Average Standard Deviation
0.680	0.220	4.40	4.53 ± 0.15
0.677	0.225	4.50	
0.674	0.235	4.70	

Fluoride Electrode

MV	From Curve	Distillate Concentration	Average Standard Deviation
24.9	2.05	4.10	4.20 ± 0.10
24.1	2.15	4.30	
24.6	2.10	4.20	

Fluoride Electrode Before Distillation

MV	From Curve	Distillant Concentration	Average Standard Deviation
75.8	0.29	0.58	0.76 ± 0.16
67.7	0.40	0.80	
64.6	0.45	0.90	

Table 15. COMPARISON OF METHODS FOR 60% TIN-40% LEAD TETRAFLUOROBORATE

Tetrafluoroborate Electrode

MV	From Curve	Average Standard Deviation
150.2	3.3	3.23 ± 0.12
150.4	3.3	
151.5	3.1	

Colorimetric Method

Absorbance	From Curve	Distillate Concentration	Average Standard Deviation
0.678	0.225	4.50	4.63 ± 0.12
0.675	0.235	4.70	
0.674	0.235	4.70	

Fluoride Electrode

MV	From Curve	Distillate Concentration	Average Standard Deviation
22.9	2.25	4.50	4.62 ± 0.11
21.8	2.35	4.70	
22.0	2.33	4.66	

Fluoride Electrode Before Distillation

MV	From Curve	Distillant Concentration	Average Standard Deviation
39.2	1.20	2.40	2.45 ± 0.05
38.0	1.25	2.50	
38.6	1.23	2.46	

Table 16. CORRELATION OF TETRAFLUOROBORATE ELECTRODE, SUBTRACTED BACKGROUND FLUORIDE CONTENT AND STANDARD ADDITION

Solution	BF_4 Electrode	Calculated Fluoride Expected	Total Fluoride	Background Subtracted	Standard Addition	Percent Difference
$NaBF_4$	3.40	2.98**	3.42	3.01		1.0
			3.15*	2.74*	3.27**	8.0*
$Cu(BF_4)_2$	4.37	3.83**	5.18	3.84		0.3
			5.00*	3.66*	3.46**	4.4*
$Sn(BF_4)_2$	3.07	2.69**	5.17	3.10		15.2
			5.13*	3.06*	2.85**	13.8*
$Pb(BF_4)_2$	4.37	3.83**	4.53	3.77		1.6
			4.20*	3.44*	3.48**	10.2*
60% Tin - 40% Lead	3.23	2.83**	4.63	2.18		23.0
			4.62*	2.17*	2.54**	23.3*

* Fluoride electrode method

** Fluoride concentration calculated from BF_4 electrode measurements

SUMMARY

The colorimetric method (SPADNS) was compared with the fluoride and tetrafluoroborate electrode methods. The calibration curve for the fluoride electrode in total ionic strength buffer was linear down to 0.2 ppm fluoride. The colorimetric calibration curve was linear down to 0.6 ppm fluoride.

In comparing fluoride concentrations before and after distillation in standard sodium fluoride solutions, there were essentially no difference in the average ppm of fluoride. However, the fluoride electrode gave slightly lower results than the colorimetric measurements. After distillation of 4 ppm tetrafluoroborate solution, the total fluoride recovered was 98% for the colorimetric method and 90% for the fluoride electrode method. In sodium tetrafluoroborate, the fluoride concentration (as calculated from the measurements of the tetrafluoroborate electrode) and the fluoride content present before distillation (as measured with the fluoride electrode) were summed to be approximately equal to the total colorimetric fluoride content. Among copper, tin, lead, and 60% tin - 40% lead tetrafluoroborates, the tin and the 60-40 mixture gave the largest difference in fluoride content when comparing the tetrafluoroborate electrode method with the colorimetric fluoride content minus fluoride electrode content before distillation. The standard addition method also compared favorably with the background subtracted fluoride content from the fluoride electrode.

Table 17. STANDARD ADDITION METHOD

Solutions	Average Potential Differences	Concentrations, ppm BF_4
$NaBF_4$	44.60	3.74
$Sn(BF_4)_2$	6.63	3.26
$Cu(BF_4)_2$	5.63	3.95
$Pb(BF_4)_2$	5.60	3.98
60% $Sn(BF_4)_2$ - 40% $Pb(BF_4)_2$	7.33	2.90

PHASE III

This phase involved the feasibility of using both the fluoride and fluoroborate electrode to observe the hydrolysis of fluoroborate in aqueous solution. Since fluoroborate is expected to give rise to fluoride upon hydrolysis (8,9,10,11) the fluoride electrode would measure the amounts of fluoride formed. Because the hydrolysis appeared to be very slow at 25°C and at high concentrations (1000 ppm), a concentration of 4 ppm was observed at 40°C. Temperatures above 50°C were not recommended for the tetrafluoroborate electrode.

Calibration curves were constructed for both electrodes at 40°C. The data are presented in Table 18. In Table 19, potential - time data are presented for tetrafluoroborate in water. The pH was also recorded because pH affects both electrodes to a certain extent. However, the fluoride electrode was most affected. From Table 19, the pH and the tetrafluoroborate concentration were decreasing, and the fluoride concentration was somewhat increasing. After 12 days, it appeared as if only 40% of tetrafluoroborate was loss at 4 ppm and about 20% was loss at 8 ppm. However, this can not be taken too seriously because of errors involving pH and limited samples. After approximately 24 hours, a white deposit was noted in the polyethylene cell. This was not further investigated.

Clark and Jones (12) used sodium citrate to quench the reaction after aliquots were taken in his study of catalyzed hydrolvsis of tetrafluoroborates. Then, the solutions were buffered. A buffer probably should be used with care. Care should be taken to make sure the buffer does not interfere with the reaction or electrode measurements. A buffer would also raise the detection limit for the liquid ion exchange tetrafluoroborate electrode.

Table 18. CALIBRATION CURVES DATA AT 40°C

BF_4 Concentration, ppm	Average Potential MV	F Concentrations, ppm	Average Potential, MV
0.5	210.3	0.01	188.4
1.0	203.1	0.1	137.3
5.0	162.4	1.0	66.7
10.0	145.1	10.0	8.2
100.0	83.5		

SUMMARY

In the hydrolysis of tetrafluoroborate, the tetrafluoroborate concentration and the pH were decreasing, and the fluoride concentration was increasing. The use of the tetrafluoroborate electrode and fluoride electrode together to determine the hydrolysis concentrations became a problem as the pH decreased. The use of a buffer in some manner may eliminate one aspect of the problem. But, a buffer probably would cause the tetrafluoroborate electrode not to respond below 2 ppm.

Table 19. POTENTIAL - TIME DATA FOR TETRAFLUOROBORATE IN WATER AT 40°C

Time, hours	BF_4 MV	Concentration, ppm	F MV	Concentration, ppm	pH
0	171.5	3.4	132.2	0.12	5.483
24	168.2	3.9	126.5	0.14	5.028
48	169.2	3.9	128.4[a]	0.13	4.783
72	168.6	3.9	87.9	0.54	4.483[a]
96	171.9	3.4	89.4	0.52	4.618
120	171.5	3.4	84.9	0.60	4.506
144	172.2	3.4	76.6	0.82	4.461
168	175.3	2.9	62.4	1.40	4.355
192	175.2	2.9	74.0	0.90	4.299
240	179.2	2.5	67.9	1.10	4.204
264	178.8	2.5	26.4[a]	5.00	4.178
288	180.1	2.4	43.6	2.60	4.103
312	182.3	2.3	50.1	2.10	4.096

[a]appear to be artifacts

SECTION VI

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